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CLAIMS

[Claim(s)]

[Claim 1] Refrigerating machine oil which consists of mixture of the following (a) and the weight ratios 20:80-99:1 of the (b) component.

(a) Complex ester of the mixed carboxylic acid and neopentyl polyol which are monocarboxylic acid in which it becomes from the mixture of the monocarboxylic acid of carbon numbers 5-14, and the dicarboxylic acid of carbon numbers 4-10, and more than 50 mol % has a branching alkyl group.

(b) Alkylbenzene one piece or whose kinematic viscosity [in / it has two pieces and / 40 degrees C] is 5-50cSt about the straight chain of carbon numbers 9-24, or the alkyl group of branching.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the refrigerating machine oil excellent in compatibility with chlorofluorocarbon, chlorofluorocarbon-proof stability, electric insulation, lubricity, etc. suitable for the refrigerator which uses hydrogen content chlorofluorocarbon, such as chlorofluorocarbon R-134a, as a refrigerant in detail about refrigerating machine oil.

[0002]

[Description of the Prior Art] Chlorofluorocarbon R-11 (trichloromonofluoromethane), chlorofluorocarbon R-12 (dichlorodifluoromethane), chlorofluorocarbon R-22 (monochlorodifluoromethane), etc. are used for the refrigerator as a refrigerant. However, we begin to be anxious about the adverse effect to the ozone layer of the chlorofluorocarbon which contains these chlorine in recent years, and according to the Montreal Protocol revised in 1990, abolition and chlorofluorocarbon R-22 will also convert chlorofluorocarbon R-11 and R-12 into the chlorofluorocarbon more desirable than an environment top by 2020 - 2040 by 2000. In connection with this, chlorofluorocarbon R-134a (1, 1, 1, 2-tetrafluoro ethane) whose ozone modulus of rupture is 0 as a substitute attracts attention. However, chlorofluorocarbon R-134a has the problem that it does not melt in the refrigerating machine oil of the conventional straight-mineral-oil system. Alkylbenzene is known as a synthetic lubricating oil excellent in chlorofluorocarbon-proof stability for refrigerating machine oil. That is, although the refrigerating machine oil which mixed alkylbenzene with the base oil of independent or others is indicated by JP,57-177096,A, JP,57-177097,A, JP,57-202389,A, and JP,61-62596,A, these are dramatically deficient in compatibility with chlorofluorocarbon R-134a. On the other hand, although the refrigerating machine oil which mixed the polyalkylene glycol with the base oil of independent or others is indicated by JP,57-63395,A, JP,59-117590,A, JP,1-115999,A, and JP,2-158693,A, since hygroscopicity is large, an activity is difficult [a polyalkylene glycol has good compatibility with chlorofluorocarbon R-134a, and] for the application of the electric refrigerator with which high electric insulation is demanded.

[0003]

[Problem(s) to be Solved by the Invention] This invention aims at offering refrigerating machine oil excellent in the engine performance demanded as a lubricating oil for refrigerators which uses chlorofluorocarbon R-134a as a refrigerant, for example, compatibility with chlorofluorocarbon, chlorofluorocarbon-proof stability, electric insulation, lubricity, etc.

[0004]

[Means for Solving the Problem] This invention is refrigerating machine oil which consists of mixture of the following (a) and the weight ratios 20:80-99:1 of the (b) component.

- (a) Complex ester of the mixed carboxylic acid and neopentyl polyol which are monocarboxylic acid in which it becomes from the mixture of the monocarboxylic acid of carbon numbers 5-14, and the dicarboxylic acid of carbon numbers 4-10, and more than 50 mol % has a branching alkyl group.
- (b) Alkylbenzene one piece or whose kinematic viscosity [in / it has two pieces and / 40 degrees C] is 5-50cSt about the straight chain of carbon numbers 9-24, or the alkyl group of branching.

[0005] (a) As an example of the monocarboxylic acid which has the straight chain alkyl group which constitutes the complex ester of a component, a valeric acid, a caproic acid, oenanthic acid, a caprylic acid, pelargonic acid, a capric acid, undecanoic acid, a lauric acid, a tridecane acid, a myristic acid, etc. are mentioned. As an example of the monocarboxylic acid which has a branching alkyl group, 2,2-dimethyl propane acid, 2, and 2-dimethyl butanoic acid, iso oenanthic acid, 2-methyl-2-ethyl butanoic acid, 2-ethylhexanoic acid, an isooctane acid, 3,5,5-trimethylhexanoate, an iso decanoic acid, iso dodecanoic acid, an iso myristic acid, etc. are mentioned. These monocarboxylic acid may be used independently, and may mix and use two or more sorts. More than 50 mol % of a mixed carboxylic acid is monocarboxylic acid which has a branching alkyl group. Compatibility with chlorofluorocarbon R-134a of refrigerating machine oil worsens that the carbon number of monocarboxylic acid is four or less, and the fluidity in the low temperature of refrigerating machine oil worsens that a carbon number is 15 or more. Compatibility with chlorofluorocarbon R-134a of refrigerating machine oil worsens that the monocarboxylic acid which has a branching alkyl group is less than [50 mol %]. As an example of the dicarboxylic acid of carbon numbers 4-10, an adipic acid, an azelaic acid, a sebacic acid, etc. may be mentioned, you may use it independently, and two or more sorts may be mixed and used.

[0006] As an example of neopentyl polyol, neopentyl glycol, trimethylolethane, trimethylol propane, pentaerythritol, dipentaerythritol, etc. may be mentioned, you may use it independently, and two or more sorts may be mixed and used.

[0007] (a) Under existence of Lewis acid catalysts, such as proton acid catalysts, such as a sulfuric acid and an alkyl sulfonic acid, and tin chloride, a titanium chloride, the complex ester of a component can esterify the mixture and neopentyl polyol of monocarboxylic acid and dicarboxylic acid directly by the usual approach, and can manufacture them. Moreover, it can refine by the usual approaches, such as alkali deoxidation and distillation.

[0008] (b) The alkylbenzene of a component is JIS. C It is [which is specified by 2320] for electrical insulation oils (two sorts of No. 1-4), and the kinematic viscosity in 40 degrees C is 5-50cSt, the monochrome which has the straight chain of carbon numbers 9-24 or the alkyl group of branching, or dialkyl benzene is used as a principal component, and the heavy alkylate which is a by-product at the time of detergent raw material manufacture as an example is mentioned. If the thing of the above-mentioned definition out of range is used, chlorofluorocarbon-proof stability or lubricity will worsen.

[0009] Although the complex ester of the (a) component and the alkylbenzene of the (b) component are mixed and used for the refrigerating machine oil of this invention in the range of the weight ratios 20:80-99:1, compatibility with chlorofluorocarbon R-134a worsens that this ratio is less than 20. Moreover, since the viscosity of refrigerating machine oil will become high if 99 is exceeded, it is not desirable.

[0010] The refrigerating machine oil of this invention may be used mixing with the refrigerating machine oil which consists of the straight mineral oil of the conventional naphthene or paraffin series, even if it uses it independently. However, when mixing and using it, it is desirable that the refrigerating machine oil of this invention is 50% of the weight or more of the whole. Compatibility with chlorofluorocarbon R-134a worsens that it is less than 50 % of the weight.

[0011]

[Effect of the Invention] The refrigerating machine oil of this invention is excellent in engine performance, such as compatibility with chlorofluorocarbon R-134a, chlorofluorocarbon-proof stability, electric insulation, and lubricity, and can be used for various kinds of refrigerators. Moreover, since it has the outstanding electric insulation, especially, it is suitable for the refrigerating machine oil for electric refrigerators, and it is possible to operate a refrigerator over a long period of time, and maintenance control becomes easy.

[0012]

[Example] Hereafter, an example explains this invention.

Composition of ester; a cooling pipe with *****, a thermometer, and nitrogen gas entrainment tubing were attached to the 1l. four glass opening flask, the mixed carboxylic acid shown in a table 1 and 500g of neopentyl polyols were taken by carboxyl group:hydroxyl-group = 1.1:1 (equivalent ratio), and it

reacted at 220 degrees C for 8 hours. The acquired resultant was distilled by 230 degrees C and 0.1mmHg using the thin film distillation machine (WFE2-03 Shinko Pantec Co., Ltd.), and the ester of a-g of a table 1 was obtained. The raw material of ester, the acid number of the obtained ester, and a hydroxyl value are shown in a table 1.

[0013]

[A table 1]

表 1

	エ ス テ ル 原 料 (モル%)	本 発 明				比 較		
		a	b	c	d	e	f	g
カ ル ボ ン 酸	イソヘブタン酸 (C ₄ H ₉ COOH) エクソン化学(株)			60				
	イソオクタン酸 (C ₈ H ₁₇ COOH) エクソン化学(株)		63					
	2-エチルヘキサノ酸 (C ₈ H ₁₇ COOH) 協和醗酵工業(株)	86						
	イソノナン酸 (ヘキストジヤパン(株))				57			
	エナント酸 (ヘブタン酸 アトケム・ジヤパン(株))						43	
	カプリル酸 (NAA-82 日本油脂(株))						42	
	ペラルゴン酸 (Emery Industries)			26		100		
	カプリン酸 (NAA-102 日本油脂(株))				32			
	ラウリン酸 (NAA-122 日本油脂(株))		32					
	オレイン酸 (NAA-34 日本油脂(株))							100
ア グ リ ン 酸	アジピン酸 (関東電化工業(株))	14		14				
	アゼライン酸 (片山化学工業(株))		5					
	セバシン酸 (豊国製油(株))				11		15	
	ネオペンチルグリコール (広栄化学工業(株))	100	65			100		
	トリメチロールプロパン (広栄化学工業(株))			100	100		100	
	ペンタエリスリトール (広栄化学工業(株))		35					100
	酸価 (KOHmg/g)	0.1	0.3	0.2	0.4	0.1	0.3	0.2
	水酸基価 (KOHmg/g)	3.7	3.1	2.9	4.3	2.0	3.8	4.4

[0014] The ester and alkylbenzene of a table 1 were mixed and this invention and comparative sample A - TE were prepared. The description is shown in a table 2.

[0015]

[A table 2]

	試料	混合物原料（重量%）									性 状		
		エステル						アルキルベンゼン		鉱油	40℃動粘度 （c S t）	流動点 （℃）	
		a	b	c	d	e	f	g	h ¹⁾	i ²⁾			j ³⁾
本 発 明	ア	50							50			18.4	-35.0
	イ		40							60		38.5	-30.0
	ウ			70						30		152.5	-30.0
	エ				20				80			45.3	-35.0
	オ	75								25		16.0	-40.0
	カ			25					75			72.3	-30.0
	キ		20	20					60			65.1	-32.5
	ク	30			30					40		35.2	-30.0
	ケ		40		20				40			46.3	-32.5
	コ		10		10				35		45	68.3	-35.0
比 較	サ	5								95		28.9	-32.5
	シ			15					85			43.3	-30.0
	ス								50	50		32.1	-27.5
	セ					50				50		17.2	-25.0
	ソ							60	40			44.3	-20.0
	タ						10		90			22.1	-25.0
	チ		10	10					20		60	65.3	-35.0
	ツ	ポリアルキレングリコール A ⁴⁾										54.8	-42.5
	テ	ポリアルキレングリコール B ⁵⁾										102.2	-35.0

- 注 1) 重質アルキレート ABA-SH (三菱油化(株))
 2) 重質アルキレート ABA-H (三菱油化(株))
 3) ナフテン系鉱物油 スニソ4GS (日本サン石油(株))
 4) LB-300 (ユニオンカーバイドケミカル社)
 5) LB-550 (ユニオンカーバイドケミカル社)

[0016] The following trial was performed as assessment of the refrigerating machine oil shown in a table 2.

Compatibility trial; the sealed tube of 0.5g of samples and R-134a2 g chlorofluorocarbon which were shown in a table 2 was put in and carried out to Pyrex tubing (the inner mold of 6mm, thickness of 2mm), and this was investigated [cooling or] at the rate of 1 degree C/m for whether temperature up is carried out and it separates into a bilayer at 70 degrees C and -30 degrees C. The case where there were 70 degrees C and -30 degrees C of no separation was made as O, and except [its] was made into x. A result is shown in a table 3.

Electric insulation trial; it is JIS about the sample shown in a table 2. C The volume resistivity was measured at 80 degrees C by the approach of 2101. A result is shown in a table 3.

Chlorofluorocarbon-proof soundness test; it examined by the sealed tube test. 0.5ml of samples shown in a table 2, a lead bar (the diameter of 3mm, die length of 25mm), and reinforcing bars (the diameter of 3mm, die length of 25mm) were put into Pyrex tubing (the bore of 6mm, thickness of 2mm), and after putting in and carrying out the sealed tube of the R-134a2 ml chlorofluorocarbon in a -60-degree C cooling bath subsequently, heating for 15 days was performed at 180 degrees C. The existence of measurement of the hue before and behind a trial (iodine methanol hue) and sludge generating was observed. The value of a hue (hue value before the hue value-trial after a trial) and the existence of sludge generating are shown in a table 3.

A lubricative trial; a Soda style walk testing machine performed the friction test. After examining for rotational-speed 220RPM, and turnover time 15 minutes on condition that 3kg/cm² of load loads, and a room temperature (20 degrees C), the abrasion was investigated, and the abrasion made less than 0.6mm O, and made ** and 0.65mm ** x for 0.6-0.65mm. A result is shown in a table 3.

[0017]

[A table 3]

	試料	相溶性	電気絶縁性 体積抵抗率 ($\Omega \cdot \text{cm}$)	耐フロン安定性		潤滑性
				試験前後の 色相差	スラッジの 有無	
本発明	ア	○	8.2×10^{12}	0	無	○
	イ	○	1.1×10^{13}	0	無	○
	ウ	○	6.8×10^{12}	1	無	○
	エ	○	1.5×10^{13}	0	無	○
	オ	○	6.3×10^{12}	0	無	○
	カ	○	1.6×10^{13}	0	無	○
	キ	○	1.2×10^{13}	1	無	○
	ク	○	8.9×10^{12}	1	無	○
	ケ	○	9.4×10^{12}	1	無	○
	コ	○	1.4×10^{13}	0	無	○
比較	サ	×	1.8×10^{13}	1	無	△
	シ	×	2.2×10^{13}	0	無	○
	ス	×	3.3×10^{14}	1	無	×
	セ	×	7.4×10^{12}	2	無	○
	ソ	×	9.2×10^{12}	3	無	○
	タ	×	5.8×10^{12}	2	無	△
	チ	×	1.5×10^{13}	1	無	△
	ツ	○	$1 \times 10^7 >$	2	有	×
	テ	○	$1 \times 10^7 >$	2	有	×

[0018] Bilayer separation temperature with chlorofluorocarbon R-134a is 70 degrees C or more and -30 degrees C or less, and each of sample A of this invention - KO has good compatibility so that clearly from the result of a table 3. Moreover, a volume resistivity is 5×10^{12} or more, and electric insulation is excellent. Furthermore, the hue change before and behind a trial is all as small as 0-1, there is no generating of a sludge, and chlorofluorocarbon-proof stability is excellent in the chlorofluorocarbon-proof soundness test. The abrasion of a lubricative trial is also as small as 0.6mm or less, and lubricity is excellent. On the other hand, sample SA of a comparison of this invention out of range - TE are inferior in compatibility with chlorofluorocarbon, electric insulation, chlorofluorocarbon-proof stability, and lubricative either.